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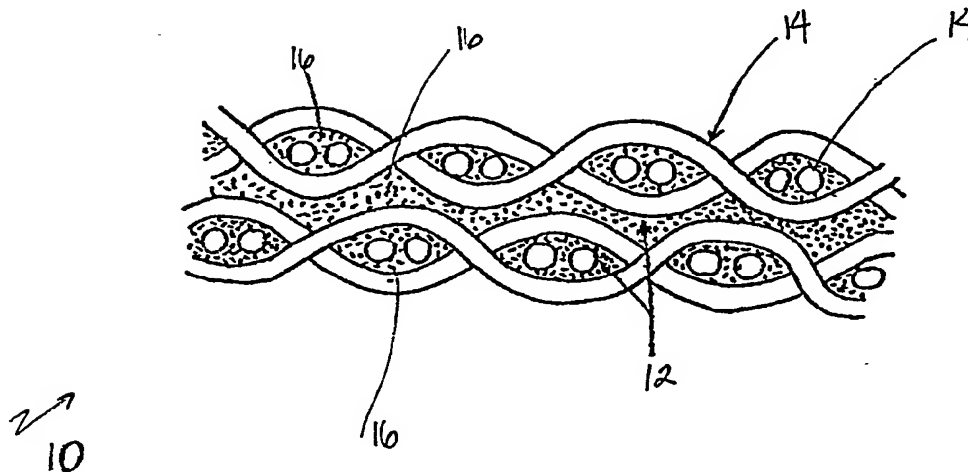
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(57) Abstract

The invention features various composites containing, e.g., carbon fibrils and methods for preparing these composites.

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COMPOSITES AND METHODS FOR MAKING SAME

Background of the Invention

This invention relates to composites and methods for preparing them.

This application is a continuation-in-part of Snyder
5 et al., U.S.S.N. 149,573 entitled "Carbon Fibrils" filed
January 28, 1988 which is assigned to the same assignee as
the present application and hereby incorporated by
reference.

Various processes exist for dispersing solid
10 fillers (e.g., fibrous or particulate fillers) in solid or
liquid matrices to form composite structures. These
processes include compounding the filler-matrix mixture
using blade mixers, high shear Waring-type blenders, roll
mills, dough mixers, or internal Brabender-type mixers.

15 Reaction injection molding ("RIM") is a molding
process in which one or more liquid or blending reactants
are metered separately to a mixing head which combines them
e.g., by high-impingement mixing. The mixture then is
injected into a mold where it polymerizes to form a molded
20 part. In structural reaction injection molding ("SRIM"),
which is often referred to as reinforced reaction injection
molding ("RRIM"), reinforcements such as chopped glass
fiber or particulate mineral fillers are added to the
mixture prior to molding. In another type of SRIM process,
25 a low viscosity, partially polymerized RIM composition is
injected into a mold filled with woven fiber mat, and the
resulting composition molded. In both the RIM and SRIM
processes, the molded parts are coated prior to use to
provide ultraviolet protection and to match other parts.

30 A second type of molding process involves premix.
Premix is a molding composition prepared prior to and
apart from the molding operation which contains all the

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components necessary for molding, e.g., resin, reinforcing agents, fillers, catalysts, release agents, etc. One type of premix is called sheet molding compound ("SMC"). SMC is a thin, semi-tacky sheet of thermosetting resin typically reinforced with chopped or continuous strand glass fibers. The sheet can be molded to form a variety of parts using, e.g., matched die molding techniques. A second type of premix is called bulk molding compound ("BMC"). BMC is prepared in the form of a putty that can be directly molded. It can also be extruded in the form of a bar or log to facilitate handling. Like the RIM and SRIM molded products, the molded premix products also are often coated prior to use.

Various types of composites are also known. For example, polymer-based electrically conductive composites (e.g., in the form of coatings or inks) are known. These composites are rendered electrically conductive by incorporating an electrically conductive additive.

Hybrid composites are structures in which a matrix is reinforced with more than one type of reinforcement. The reinforcing agent present in the largest volume fraction (compared to the other reinforcing agents) is referred to as the primary reinforcing agent, while the remaining reinforcing agents are referred to as secondary reinforcing agents.

Elastomers have also been filled with a variety of materials. Such materials are used to improve the mechanical or electrical properties of the elastomer matrix, or to reduce cost.

Friction materials are materials which convert an applied force to heat in order to dissipate the force. Examples of applications of such materials include brakes,

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automatic transmission disks, and clutches. Reinforced organic polymers have been used as friction materials.

Carbon fibrils are carbon filaments having diameters less than 500 nanometers. Examples of particular carbon fibrils and methods for preparing them are described in Snyder et al., U.S.S.N. 149,573 ("Carbon Fibrils") filed January 28, 1988; Tennent, U.S. Pat. No. 4,663,230 ("Carbon Fibrils, Method for Producing Same and Compositions Containing Same"); Tennent et al., U.S.S.N. 871,676 filed June 6, 1986 ("Novel Carbon Fibrils, Method for Producing Same and Compositions Containing Same"); Tennent et al., U.S.S.N. 871,675 filed June 6, 1986 ("Novel Carbon Fibrils, Method for Producing Same and Encapsulated Catalyst"); Mandeville et al., U.S.S.N. 285,817 filed December 16, 1988 ("Fibrils"); and McCarthy et al., U.S.S.N. 351,967 filed May 15, 1989 ("Surface Treatment of Carbon Microfibers"), all of which are assigned to the same assignee as the present application and are hereby incorporated by reference in their entirety.

Summary of the Invention

Compounding Process

This invention features a compounding process for preparing a composite that includes the steps of introducing one or more fillers and a matrix material into a stirred ball mill, and subjecting the fillers and matrix material to a combination of shear and impact forces under reaction conditions including reaction time sufficient to reduce the size of agglomerates formed by the fillers to a value below a pre-determined value to disperse the fillers throughout the matrix material.

In preferred embodiments, the pre-determined value of the agglomerate size is no greater than 1000 times the size of the filler, more preferably no greater than 100

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times, even more preferably no greater than 10 times. One or more of the characteristic dimensions of the filler (which is a measure of its size) preferably is less than 1 μm , more preferably less than 0.1 μm .

5 A viscosity modifier (i.e. a material that modifies the intrinsic viscosity of the matrix-filler mix to facilitate dispersion) is preferably added to the stirred ball mill. Preferred viscosity modifiers include both materials that are removed following the dispersion step,
10 e.g., solvents, and materials that are retained following the dispersion step; an example of the latter type of viscosity modifier is a reactive diluent that chemically reacts with the matrix material. In additional preferred embodiments, one or more milling media (i.e. a particulate
15 material that facilitates dispersion by supplying additional impact force) is added to the stirred ball mill.

Preferred fillers include whiskers (i.e. single crystal fibers), discontinuous fibers, particulate fillers, and carbon fibrils. The fibrils preferably are tubes
20 having graphitic layers that are substantially parallel to the fibril axis. One aspect of substantial parallelism is that the projection of the graphite layers on the fibril axis extends for a relatively long distance in terms of the external diameter of the fibril (e.g., at least two fibril
25 diameters, preferably at least five diameters), as described in Snyder et al., U.S.S.N. 149,573. These fibrils preferably are also free of a continuous thermal carbon overcoat (i.e. pyrolytically deposited carbon resulting from thermal cracking of the gas feed used to
30 prepare the fibrils). The fibrils preferably have diameters between 3.5 and 75 nanometers, inclusive, and a length to diameter ratio of at least five. Also preferred are fibrils having this morphology in which the outer

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surface of the graphitic layers is bonded to a plurality of oxygen-containing groups (e.g., a carbonyl, carboxylic acid, carboxylic acid ester, epoxy, vinyl ester, hydroxy, alkoxy, isocyanate, or amide group), or derivatives thereof (e.g., a sulfhydryl, amino, or imino group).

Preferred matrix materials include metal powder, ceramic powder (e.g., glass powder), thermoplastic resins, thermoset resins, and elastomers, and matrix materials which are in the form of liquids. Preferred thermoplastic resins include thermoplastic polyester (e.g., polyethylene terephthalate), polyurethane, polyether ether ketone, polyether sulfone, polyether imide, polyamide (e.g., nylon), and polyurea resins. Preferred thermoset resins include phenolic, epoxy, thermosetting polyurethane, thermosetting polyester (e.g., alkyd), polyimide, bismaleimide, polycyclopentadiene, and vinylacrylimide (such as the Arimix resins commercially available from Ashland Chemical Co., Columbus, Ohio). Preferred elastomers include styrene-butadiene rubber, natural rubber, ethylene-propylene-diene monomer (EPDM) rubber, silicone rubber, polybutadiene (both cis and trans 1,4 and 1,2-polybutadiene), polyisoprene, neoprene, chloroprene, fluoroelastomers (e.g., fluorinated polyethylene), and urethane elastomers.

When the matrix material is a thermoplastic resin, the compounding process preferably includes cooling the contents of the stirred ball mill to a temperature at which the matrix material becomes brittle prior to the dispersion step, and maintaining that temperature throughout the dispersion step.

The invention also features a composite prepared according to the above-described process.

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The invention creates composites in which the filler is substantially uniformly dispersed throughout the matrix material, even when the mean filler diameter is on the order of a micron or less, leading to improved composite properties, e.g., electrical, optical, mechanical, and magnetic properties. The degree of uniformity (as measured by the size of the filler agglomerates) can be tailored to the particular application for which the composite is intended by adjusting the milling time.

The invention also makes it possible to co-disperse a variety of fillers having different diameters and/or shapes in a matrix. Moreover, the invention obviates the need for pre-treating the filler surface or adding chemical dispersants to achieve good filler dispersion throughout the matrix.

Composites for Electrostatic Overcoating

This invention features a composite that includes a matrix into which carbon fibrils are incorporated, the amount of the fibrils being sufficient to permit the composite to be directly electrostatically overcoated (i.e. without applying a primer coat first).

In one aspect, the composite includes a reaction injection molded matrix into which carbon fibrils have been incorporated.

In a second aspect, the composite includes the molded product of a premix that includes a resin matrix into which carbon fibrils have been incorporated.

In preferred embodiments, the premix is a sheet molding compound or a bulk molding compound. The electrical conductivity of the composite preferably is greater than the electrical conductivity of a composite in which the same matrix is filled with an equivalent amount of carbon black. The amount of fibrils in the composite preferably

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is sufficient to impart to the composite an electrical conductivity sufficiently high to permit direct electrostatic overcoating. Also preferred are composites in which the amount of fibrils is sufficient to dissipate static electricity. Preferably, the amount is less than or equal to 20% by weight (based on resin), more preferably less than or equal to 4% by weight.

The fibrils preferably are tubes having graphitic layers that are substantially parallel to the fibril axis. One aspect of substantial parallelism is that the projection of the graphite layers on the fibril axis extends for a relatively long distance in terms of the external diameter of the fibril (e.g., at least two fibril diameters, preferably at least five diameters), as described in Snyder et al., U.S.S.N. 149,573. These fibrils preferably are also free of a continuous thermal carbon overcoat (i.e. pyrolytically deposited carbon resulting from thermal cracking of the gas feed used to prepare the fibrils). The fibrils preferably have diameters between 3.5 and 75 nanometers, inclusive, and a length to diameter ratio of at least five. Also preferred are fibrils having this morphology in which the outer surface of the graphitic layers is bonded to a plurality of oxygen-containing groups (e.g., a carbonyl, carboxylic acid, carboxylic acid ester, epoxy, vinyl ester, hydroxy, alkoxy, isocyanate, or amide group), or derivatives thereof (e.g., a sulfhydryl, amino, or imino group).

Preferred matrix materials include thermoplastic resins (e.g., polyamide, polyurethane, polyurea, or an elastomer) and thermoset resins (e.g., polydicyclopentadiene, polyester, thermosetting polyurethane, or epoxy resins, or vinylacrylimide resins (such as the Arimix resins commercially available from

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Ashland Chemical Co., Columbus, Ohio). Resin mixtures may also be used. Either composite preferably is molded in the form of an automotive part for a car, truck, or bus.

In a third aspect, the invention features a
5 composite in a form suitable for reaction injection molding that includes one or more liquid reactants capable of polymerizing to form a reaction injection molded matrix and carbon fibrils.

In a fourth aspect, the invention features a premix
10 that includes a resin into which carbon fibrils are incorporated.

In preferred embodiments, the liquid reactants include one or more polyols, polyisocyanates, or polyamines. The premix preferably is a bulk molding compound or a sheet
15 molding compound. The amount of fibrils is preferably less than or equal to 20% by weight, more preferably less than or equal to 4% by weight. Preferred fibrils and resins are those described above.

The invention also features methods for preparing
20 the above-described composites.

The reaction injection molded composite is prepared by a method that includes mixing the fibrils with liquid reactants capable of polymerizing to form the matrix; introducing the mixture into a mold; and molding the
25 mixture under reaction conditions including pressure and temperature to prepare the composite in the form of a molded part.

The sheet molding compound composite is prepared by a method that includes mixing the fibrils with a resin and
30 forming the mixture into a sheet. The bulk molding compound composite is prepared by a method that includes mixing the fibrils with a resin to form a putty suitable for molding. Both methods preferably include a molding

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step in which the composite is prepared in the form of a molded part under reaction conditions that include temperature and pressure.

5 The molded parts prepared according to the above-described methods are preferably directly electrostatically coated once molding is complete.

10 The invention provides reaction injection molded composites and molded composites prepared from premix (e.g., sheet molding compound or bulk molding compound) that are electrically conductive at relatively low fibril loadings. This enables molded parts prepared from the composites to be electrostatically coated just as metal parts currently are, thereby eliminating the need for applying a conductive primer coat in a separate application.

15 Further advantages that the fibrils provide include good mechanical properties (e.g., hardness and impact strength) and the ability to use reduced amounts of additives such as flame retardants. The fibrils also provide inherent EMI shielding.

20 The use of fibrils offers several processing advantages as well, including good batch to batch consistency with respect to electrical and mechanical properties. In the case of RIM processing, the fibrils, due to their small size, do not plug small lines and orifices in the processing equipment at the low fibril loadings used. Moreover, the fibrils need not become preferentially oriented during processing; thus, they do not contribute to part warpage. In the case of SMC, the increase in viscosity due to the fibrils makes it possible

25 to eliminate thickeners needed to form the tacky sheet.

30 Electrically Conductive Coatings and Inks

This invention features an electrically conductive composite in a form suitable for applying to the surface of

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a substrate that includes a polymeric binder into which carbon fibrils are incorporated.

In preferred embodiments, the composite is in the form of a powder or liquid coating. The amount of fibrils in the coating preferably is sufficiently high to permit a substrate to which the coating is applied to be electrostatically overcoated directly. Preferably, the amount is less than or equal to 15% by weight (based on resin), more preferably between 0.5 and 10% by weight.

Even more preferred are coatings in which the amount of fibrils is between 1 and 4% by weight. The coatings may include one or more pigments.

In another preferred embodiment, the coating is in the form of a resistive ink suitable for screen printing on the surface of a substrate to form an electronic component. Preferably, the amount of fibrils in the resistive ink is sufficient to decrease bulk resistivity of the binder to a value between 10^{-2} and 10^6 ohm cm (more preferably between 10^{-1} and 10^4 ohm cm) when applied to a substrate. The preferred amount of fibrils is between 1 and 30% by weight.

In another preferred embodiment, the coating further comprises electrically conductive graphite or metal particles (e.g., silver flakes, metal-coated chopped fibers, or metal powder) and is in the form of conductive ink suitable for printing on the surface of a substrate; the amount of fibrils in the ink is sufficient to decrease the bulk resistivity of the particle-filled binder (measured in the absence of carbon fibrils) by a predetermined amount when applied to a substrate. Preferably, the bulk resistivity of the particle-filled binder is greater than 1 ohm cm and the amount of fibrils is sufficient to reduce the bulk resistivity to less than 1

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ohm cm. Even more preferred are conductive inks in which the bulk resistivity of the particle-filled binder is greater than 10^{-1} ohm cm and the amount of fibrils is sufficient to reduce the bulk resistivity to less than 10^{-1} ohm cm. The preferred amount of fibrils is between 20 and 50% by weight.

The fibrils preferably are tubes having graphitic layers that are substantially parallel to the fibril axis. One aspect of substantial parallelism is that the projection of the graphite layers on the fibril axis extends for a relatively long distance in terms of the external diameter of the fibril (e.g., at least two fibril diameters, preferably at least five diameters), as described in Snyder et al., U.S.S.N. 149,573. These fibrils preferably are also free of a continuous thermal carbon overcoat (i.e. pyrolytically deposited carbon resulting from thermal cracking of the gas feed used to prepare the fibrils). The fibrils preferably have diameters between 3.5 and 75 nanometers, inclusive, and a length to diameter ratio of at least five.

Preferred polymeric binders include thermoplastic resins (e.g., polyethylene, polypropylene, polyamide, polyurethane, polyvinyl chloride, or thermoplastic polyester resin such as polyethylene terephthalate) and thermoset resins (e.g., a thermosetting polyester resin or an epoxy resin).

The invention also features a substrate coated with a fibril-filled electrically conductive composite. Preferably, the conductivity of the composite is sufficiently high to permit the coated substrate to be electrostatically overcoated directly. Also preferred are substrates for printed circuit boards in which the

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composite is a resistive ink printed on the substrate in the form of an electronic component (e.g., a resistor) or a conductive ink printed on the substrate in the form of a conductive trace for electrically connecting electronic components. Also featured are methods for preparing coated substrates (which are amenable to direct electrostatic coating) and for screen printing fibril-filled inks on a substrate.

The fibril-filled composites are electrically conductive at low fibril loadings. As a result, coatings and inks having predetermined resistivity values can be prepared without excessive increases in viscosity due to the added fibrils; such increases are undesirable because they make application difficult. The properties of the composites also do not vary significantly from batch to batch because the fibrils exhibit good resistance to shear degradation caused by the shear mixing used to prepare the composites. In addition, the resistivity of the composites is relatively insensitive to temperature fluctuations.

When used as a primer on a molded part (e.g., an automotive part) for subsequent electrostatic overcoating, the coatings permit direct electrostatic overcoating at lower energy, thereby reducing corona effects and providing uniform coverage. Moreover, the fibril-filled composites can be overpigmented so that the finished composite does not appear black. The coatings are also sufficiently electrically conductive to be used in combination with sacrificial anode materials on the exposed surface of a metal or molded plastic part to help prevent corrosion. When applied to plastic substrates, the coatings exhibit good mechanical adhesion and permit metal to be plated directly onto the plastic.

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Fibril-filled composites in the form of resistive or conductive inks offer additional advantages. When printed on a substrate, the resistivity of the ink and its ability to adhere to the substrate do not deteriorate due to creasing or bending of the substrate. The inks are also scuff- and scratch-resistant. In the case of conductive inks, the fibril-filled inks are lighter than inks in which the conductive filler is 100% metal particles (thereby facilitating application) and exhibit improved corrosion resistance. Moreover, the fibrils allow the resistivity of the metal particle-containing conductive inks to be fine tuned for application-specific uses, thereby achieving resistivity values not readily attainable using metal particles alone.

15 Elastomers

This invention features a composite in which carbon fibrils are incorporated in an elastomer matrix. In one aspect, the fibrils are characterized as having a morphology consisting of tubes that are free of a continuous thermal carbon overcoat (i.e. pyrolytically deposited carbon resulting from thermal cracking of the gas feed used to prepare the fibrils) and have graphitic layers that are substantially parallel to the fibril axis. One aspect of substantial parallelism is that the projection of the graphite layers on the fibril axis extends for a relatively long distance in terms of the external diameter of the fibril (e.g., at least two fibril diameters, preferably at least five diameters), as described in Snyder et al., U.S.S.N. 149,573. These fibrils preferably have diameters less than 100 nanometers, more preferably between 3.5 and 75 nanometers, inclusive, and a length to diameter ratio of between 5 and 100.

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In a second aspect, the fibrils are characterized as having a crystalline graphitic structure and a morphology defined by a fishbone-like arrangement of the graphite layers along the fibril axis. Examples of such fibrils are described in the aforementioned Snyder et al. application, U.S.S.N. 149,573 and in Geus et al., European Application No. 0 198 558 published October 22, 1986. These fibrils preferably have diameters less than 100 nanometers.

The amount of fibrils in the composite is preferably sufficiently high to permit curing of the composite by resistive or inductive heating or to permit at least one of the physical properties of the composite to be monitored electrically; preferably, this amount is less than 25 parts per 100 parts of elastomer, more preferably less than 10 parts per 100 parts of elastomer. In the case of masterbatches (i.e. fibril-filled elastomer precursors which are subsequently blended with additional elastomer in order to prepare the final composite structures), however, the amount of fibrils is preferably greater than 25 parts per 100 parts of elastomer.

Preferred elastomer matrices include natural rubber, styrene-butadiene rubber (both random and block copolymers), polyisoprene, neoprene, chloroprene, polybutadiene (both cis and trans 1,4 and 1,2-polybutadienes), fluoroelastomers (e.g., fluorinated polyethylene), silicone rubbers, and urethane elastomers. In addition to the fibrils, the elastomer preferably contains one or more fillers, e.g., carbon black, silica, or a combination thereof; the ratio of the amount of fibrils in the composite to the total amount of the fillers is at least 1:4 or better (e.g., 1:5, 1:6, etc.). The composites are preferably provided in the form of a tire or

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component thereof (e.g., tire tread or casing), seal, solution, or adhesive.

In a third aspect, the invention features a method for curing an elastomer that includes the steps of
5 preparing a composite by incorporating carbon fibrils in an elastomer matrix, the amount of the fibrils being sufficient to impart to the composite an electrical conductivity sufficiently high to permit resistive or inductive heating, and heating the composite resistively or inductively to
10 effect cure.

In a fourth aspect, the invention features a method for monitoring the physical condition of an elastomer that includes the steps of preparing a composite by
15 incorporating an electrically conductive additive in an elastomer matrix, the amount of the additive being sufficient to impart to the composite an electrical conductivity sufficiently high to permit the physical condition of the elastomer to be monitored electrically, and monitoring the electrical properties (e.g.,
20 resistivity) of the composite as an indication of the physical condition of the elastomer. In a preferred embodiment of this aspect, the electrically conductive additive includes carbon fibrils. In another preferred embodiment, the composite is in the form of a tire and the
25 the pressure inside the tire is monitored. The method is also preferably used to monitor an elastomer (e.g., in the form of a conveyor belt or hose) for the presence of rips, tears, or perforations.

In preferred embodiments of the third and fourth
30 aspects, the amount of fibrils in the composite is less than 25 parts per 100 parts elastomer, more preferably less than 10 parts per 100 parts elastomer. Preferred fibrils are those described above.

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In a fifth aspect, the invention features a method for preparing an elastomer composite that includes the steps of preparing a masterbatch by dispersing in an elastomer at least 25 parts of fibrils per 100 parts of elastomer, and compounding a predetermined portion of the masterbatch with an additional amount of an elastomer which may be the same as or different from the elastomer used to prepare the masterbatch) to prepare the composite.

Preferably, the amount of fibrils in the final composite is less than 25 parts per 100 parts elastomer, more preferably less than 10 parts. Preferred fibrils are as described above. Carbon black may also be added to the composite, either during preparation of the masterbatch or during the compounding step.

In a sixth aspect, the invention features a method for reinforcing an elastomer that includes incorporating into an elastomer matrix an amount of carbon fibrils sufficient to improve the mechanical properties of the elastomer. The fibrils are as described above for the first and second aspects of the invention.

The invention provides fibril-reinforced elastomer composites exhibiting good stiffness, tensile strength, tear strength, creep and die swell resistance, and green strength (i.e. strength prior to cure). The composites also exhibit good hardness, stress-strain properties, and abrasion resistance (even with relatively soft elastomer matrices), and have low specific gravity. The improved abrasion resistance makes it possible to achieve an advantageous balance of traction, rolling resistance, and tread wear in articles fabricated from the composites. Moreover, these advantages are achieved at low fibril loadings.

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Further advantages result from the electrical properties of the fibrils. Because the fibrils are electrically conductive, they can be used to perform the dual functions of reinforcing an elastomer matrix and at the same time rendering the matrix electrically conductive. The electrically conductive composites can be cured by resistive or inductive heating, thus avoiding the problems of thermal transfer and high cost often associated with conventional heat curing. The ability to be cured electrically makes the fibril-filled composites particularly useful as adhesives in a variety of bonding operations such as forming rubber-rubber bonds (e.g., in bonding tire treads to tire casings), rubber-metal bonds, and rubber-ceramic bonds, and in rubber repair systems for products such as tires and conveyor belts.

The electrical conductivity of the composites is also useful in applications such as the extrusion of rubber tubes, treads, and related products. In addition, the composites can be partially electrically cured to impart additional dimensional stability to the composite. The invention also makes possible the design products in which physical changes in the composite such as internal pressure can be monitored electrically. For example, the state of a tire, air spring, hose, or conveyor belt can be monitored simply and effectively.

Friction Materials

This invention features, in a first aspect, a brake or component thereof prepared from a friction material that includes a matrix into which carbon fibrils have been incorporated.

In a second aspect, the invention features a clutch or component thereof prepared from a friction material that

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includes a matrix into which carbon fibrils have been incorporated.

In a third aspect, the invention features an automatic transmission disk or component thereof prepared from a friction material that includes a matrix into which carbon fibrils have been incorporated.

In a fourth aspect, the invention features a composite in the form of a friction material that includes a matrix into which carbon fibrils have been incorporated.

In preferred embodiments, the amount of fibrils is less than or equal to 20% by weight (based on resin), more preferably between 5 and 10% by weight.

The fibrils preferably are tubes having graphitic layers that are substantially parallel to the fibril axis. One aspect of substantial parallelism is that the projection of the graphite layers on the fibril axis extends for a relatively long distance in terms of the external diameter of the fibril (e.g., at least two fibril diameters, preferably at least five diameters), as described in Snyder et al., U.S.S.N. 149,573. These fibrils preferably are also free of a continuous thermal carbon overcoat (i.e. pyrolytically deposited carbon resulting from thermal cracking of the gas feed used to prepare the fibrils). The fibrils preferably have diameters between 3.5 and 75 nanometers, inclusive, and a length to diameter ratio of at least five. Also preferred are fibrils having this morphology in which the outer surface of the graphitic layers is bonded to a plurality of oxygen-containing groups (e.g., a carbonyl, carboxylic acid, carboxylic acid ester, epoxy, vinyl ester, hydroxy, alkoxy, isocyanate, or amide group), or derivatives thereof (e.g., a sulfhydryl, amino, or imino group).

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Preferred matrix materials are carbon and thermosetting resins, e.g., phenolic, polyester, and epoxy resins. One or more additional fillers preferably are added as well. Examples of preferred fillers include
5 metal, glass, ceramic, carbon, or polyaramide fibers, or particulates such as graphite, clay, barium sulfate, diatomaceous earth, silica, magnesia, beryllia, alumina, silicon carbide, boron carbide, titanium dioxide, or carbon black. Examples of preferred applications for the friction
10 materials include clutches, automatic transmission disks, and brakes (e.g., linings for brake pads and shoes).

Articles fabricated from the friction materials prepared from fibril-containing composites exhibit good friction properties and fade resistance. These properties
15 are retained at elevated temperatures, a quality particularly useful for heavy duty applications including off-road vehicles, racing cars, heavy machinery, and automotive disc brakes which are often subjected to such temperatures. Moreover, the friction materials resist
20 spalling and cracking at elevated temperatures.

Hybrid Composites

This invention features, in a first aspect, a hybrid composite that includes a matrix into which is incorporated a primary fibrous reinforcing agent and a
25 secondary reinforcing agent uniformly dispersed throughout the matrix and randomly oriented relative to the primary reinforcing agent.

In preferred embodiments, the mean diameter of the primary reinforcing agent is at least 10 times greater than
30 the mean diameter of the secondary reinforcing agent, more preferably at least 100 times greater. The majority of agglomerates formed by the secondary reinforcing agent in

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the matrix preferably are no greater than $10\mu\text{m}$, preferably no greater than $0.5\mu\text{m}$.

The secondary reinforcing agent preferably includes carbon microfibers (i.e. carbon fibers having diameters less than or equal to one micron), whiskers (i.e. single crystal fibers), chopped fibers (i.e. discontinuous fibers whose lengths are on the order of $1/16 - 2$ inches), and particulate materials, e.g., silica or carbon black. Also preferred are carbon fibrils, preferably those which are tubes having graphitic layers that are substantially parallel to the fibril axis. One aspect of substantial parallelism is that the projection of the graphite layers on the fibril axis extends for a relatively long distance in terms of the external diameter of the fibril (e.g., at least two fibril diameters, preferably at least five diameters), as described in Snyder et al., U.S.S.N. 149,573. These fibrils preferably are also free of a continuous thermal carbon overcoat (i.e. pyrolytically deposited carbon resulting from thermal cracking of the gas feed used to prepare the fibrils). The fibrils preferably have diameters between 3.5 and 75 nanometers, inclusive, and a length to diameter ratio of at least five. The amount of the secondary reinforcing agent incorporated in the matrix preferably is less than or equal to 20% by volume, more preferably between 1 and 10% by volume.

Preferred primary reinforcing agents include continuous fibers. Examples of preferred continuous fibers include carbon, glass, ceramic (e.g., boron, alumina, or silicon carbide), and polyaramide (e.g., Kevlar) fibers. These fibers may be woven, knit, crimped, or straight. Also preferred are primary reinforcing agents which include discontinuous fibers made of the same types of materials as the continuous fibers.

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Preferred matrix materials include organic thermoset and thermoplastic resins. Examples of preferred thermoset resins include epoxy, bismaleimide, polyimide, and polyester resins. Examples of preferred thermoplastic resins include polyethylene, polypropylene, polyamide (e.g., nylon), polyurethane, polyvinyl chloride, thermoplastic polyester resin, polyether ether ketone, polyether sulfone, polyether imide, oriented polyethylene, liquid crystalline polymers, and reaction injection molded resins. Other preferred matrix materials include inorganic polymers (e.g., a polymeric inorganic oxide such as glass), metals (e.g., aluminum or titanium alloys), ceramics (e.g., Portland cement or concrete), and carbon.

In a second aspect, the invention features a hybrid composite that includes a matrix into which is incorporated a primary fibrous reinforcing agent and a secondary fibrous reinforcing agent, the primary reinforcing agent having a mean diameter that is at least 1000 times greater than the mean diameter of the secondary reinforcing agent.

In preferred embodiments of the second aspect, the secondary reinforcing agent is dispersed uniformly throughout the matrix and randomly oriented relative to the primary reinforcing agent. Preferred secondary reinforcing agents are carbon fibrils, as described above. Preferred matrix materials, primary reinforcing agents, agglomerate sizes, and amounts of secondary reinforcing agents are as described above.

The invention also features methods for preparing the hybrid composites.

The invention provides hybrid composites having properties not attainable in composites containing only primary reinforcing agents. Because the secondary reinforcing agent is randomly oriented relative to the

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primary reinforcing agent and uniformly dispersed throughout the matrix (as measured by the small agglomerate size throughout the matrix), transverse and interlaminar properties, which ordinarily are dominated by the matrix rather than the primary reinforcing agent, are improved. Moreover, because the secondary reinforcing agent is substantially smaller than the primary reinforcing agent, its incorporation into the matrix does not impair the properties of the primary reinforcing agent. In addition, dispersing the secondary reinforcing agent throughout the matrix, rather than between layers of the primary reinforcing agent, avoids disrupting or distorting the primary reinforcement weave or lay-up.

Other features and advantages will be apparent from the following description of the preferred embodiments thereof, and from the claims.

Description of the Preferred Embodiments

We first briefly describe the Figure.

The Figure is a schematic cross-sectional representation of a two-dimensional hybrid composite embodying the invention.

Compounding Process

Composites are preferably prepared by introducing the matrix material and one or more fillers into a stirred ball mill of the type conventionally used for powder comminution. In the mill, these materials are subjected to both shearing forces due to the stirring action of a mechanical rotor and impact forces due to particulate milling media of the type conventionally used for powder comminution which are added to the mill during stirring; these particulates are removed once the milling operation is over. In the case of metal and ceramic matrices, however, it is not necessary to add separate milling media

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because the matrices themselves (which are added in the form of powders) are capable of supplying the impact force.

A viscosity modifier is added to viscous matrix-filler mixes to lower the intrinsic viscosity to a value sufficiently low to permit easy milling. Viscosity modifiers are particularly useful when the matrix material is a high molecular weight thermoplastic or a partially cured thermoset resin. Examples of suitable viscosity modifiers include solvents such as water, toluene, acetone, methyl ethyl ketone (MEK), isopropanol, or mineral oil. Following the milling operation the solvent is removed, e.g., by vacuum drying, steam stripping, or freeze drying. The viscosity modifier may also be a material which becomes part of the matrix or filler once milling is complete. Examples of such modifiers include monomers called reactive diluents (e.g., styrene, triallyl cyanurate, diallylcyanurate, multi-functional acrylates, and divinylbenzene) which chemically react with the matrix material during milling. The viscosity modifier may also be built into the matrix. In such cases, the viscosity modifier may be present during manufacture of the matrix, e.g., in solutions of solution-polymerized SBR and solutions of thermoplastics obtained from the polymerization reaction.

Suitable fillers include discontinuous fibers (e.g., chopped glass or carbon fibers), whiskers (e.g., carbon or silicon carbide whiskers), particulate fillers (e.g., silica or carbon black), carbon fibrils, or a combination of any or all of these fillers. Preferably, the mean filler diameter (i.e. the diameter of the individual grains or fibers making up the filler) is on the order of a micron or less. Preferred fibrils have small diameters (preferably between 3.5 and 75 nanometers),

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graphitic layers that are substantially parallel to the fibril axis, and are substantially free of a continuous thermal carbon overcoat, as described in Tennent, U.S. Pat. No. 4,663,230; Tennent et al.; U.S.S.N. 871,675; Tennent et al., U.S.S.N. 871,676; Snyder et al., U.S.S.N. 149,573; and Mandeville et al., U.S.S.N. 285,817. These fibrils are prepared as described in the aforementioned patent and patent applications. The fibrils may also be treated to introduce oxygen-containing functional groups onto the fibril surface, as described in McCarthy et al., U.S.S.N. 351,967. Preferred matrix materials include metal and ceramic (e.g., glass) powders, and organic matrices, e.g., thermoplastic, thermoset, and elastomer resins, as described in the Summary of the Invention, above. The preparation of carbon fibril-filled elastomers is described in Barber et al., U.S.S.N. _____, entitled "Fibril-Filled Elastomers", filed concurrently with the present application and assigned to the same assignee as the present application, and is hereby incorporated by reference in its entirety. In the case of thermoplastic resins, the composites are preferably prepared by introducing the resin and fillers into the stirred ball mill, and then adding dry ice to the mill to cool the contents to a temperature at or near which the resin is transformed into a brittle solid. In this form, the resin is more easily broken up during milling, leading to more uniform dispersions. The dry ice evaporates during milling so that none is retained in the final dispersion.

The milling time determines the final size of the filler agglomerates and thus the degree of dispersion, which in turn, is a function of the end use for which the composite is targeted. For example, electrical applications, which rely on interparticle contact to

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establish a conductive network, can tolerate larger agglomerates than mechanical applications, where the agglomerates act as strength-lowering defects.

A composite in which carbon fibrils (prepared as described above) were dispersed in a styrene butadiene rubber (SBR) matrix was prepared using the above-described stirred ball milling procedure and its properties compared to a fibril-reinforced SBR matrix prepared using conventional internal mixing and roll milling compounding techniques. The results, which are shown in Table I, demonstrate that the composite prepared using the stirred ball mill exhibits superior properties.

Table I

<u>Property</u>	<u>Roll Mill</u>	<u>Ball Mill</u>
15 Ultimate Tensile Strength (MPa)	6.7	10.1
Elongation at Break (%)	255	395
Modulus at Elongation (MPa)		
20 100%	2.8	3.1
200%	5.2	5.4
300%	----	7.5
Hardness (IRHD)	64	64
Trouser Tear (KN/M)	5.4	6.0
25 Ring Fatigue (Kilocycles to failure)	12	40
DIN Abrasion:		
Loss (mm ³)	203	189
Index	95	102
30 Heat Build-up (°C)	70	65
Resistivity (Ω cm)	2190	42

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The compounding method can also be used to prepare prepregs for hybrid composites as described in Creehan et al., U.S.S.N. _____ entitled "Hybrid Composites", filed concurrently with the present application and assigned to the same assignee as the present application, and is hereby incorporated by reference in its entirety.

Composites for Electrostatic Overcoating

By way of the following examples, the preparation of sheet molding compound (SMC) composites, bulk molding compound (BMC) composites, and reaction injection molded (RIM) composites into which carbon fibrils have been incorporated are described. Preferred fibrils have small diameters (preferably between 3.5 and 75 nanometers), graphitic layers that are substantially parallel to the fibril axis, and are substantially free of a continuous thermal carbon overcoat, as described in Tennent, U.S. Pat. No. 4,663,230; Tennent et al.; U.S.S.N. 871,675; Tennent et al., U.S.S.N. 871,676; Snyder et al., U.S.S.N. 149,573; and Mandeville et al., U.S.S.N. 285,817. These fibrils are prepared as described in the aforementioned patent and patent applications. The fibrils may also be treated to introduce oxygen-containing functional groups onto the fibril surface, as described in McCarthy et al., U.S.S.N. 351,967.

Example 1 - RIM

Fibril-containing RIM composites are prepared using conventional RIM processing equipment. Such equipment typically includes a material conditioning system, a high pressure metering system, a mix head, a mold, and a mold carrier.

The material conditioning system includes tanks that hold the reactants for preparing the composite (each

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reactant being stored in a separate tank), agitators to maintain homogeneous temperature and composition conditions throughout the tanks, and a temperature control system for maintaining the proper level of dissolved gases in the
5 reactants. The fibrils are preferably pre-mixed with one or more of the reactants in an amount sufficient to result in 1-4 weight % fibrils in the final molded product. Additional tanks store additives such as pigments and catalysts, as well as any additional reinforcement, e.g.,
10 chopped glass fibers. Preferred reactants include polyols and polyisocyanates (for preparing polyurethane matrices) and polyamines and polyisocyanates (for preparing polyurea matrices).

The metering system, which typically consists of,
15 e.g., high pressure axial or radial piston pumps or lance-displacement cylinders, meters the proper amount of reactants, fibrils, and any additional fillers to the mixing head. The mixing head contains a chamber in which the reactants and fillers are mixed by direct impingement
20 at pressures between, for example, 1500 and 3500 psi. When mixing is complete, the mixture is transported to a mold where the reactants polymerize to form the final part. Suitable mold constructions include machined steel or aluminum, cast aluminum or kirksite, spray metal or
25 electroplated shells, and filled epoxy resin. Typical in-mold pressures during polymerization are 25-100 psi. The molding temperature varies according to the particular reactants being used, as one of ordinary skill in the art will readily appreciate. In the case of polyurethane -
30 forming reactants, the mold temperature is about 130°F (\pm 70°F). A mold carrier orients the mold, provides a clamping force to overcome the in-mold pressure, opens and closes the mold, and positions the mold for removal of the

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finished part, cleaning, and preparation for the next molding operation.

The fibril-containing RIM composites are useful in a wide variety of molded industrial and consumer products.

5 They are particularly useful in automotive parts, e.g., bumpers, trim parts, fascia, integral window seals, steering wheels, armrests, protective covers, and body panels for cars, trucks, or buses. The parts are coated prior to use. By incorporating carbon fibrils, the parts
10 can be electrostatically coated, making fabrication compatible with the processing of metal parts.

Example 2 - SMC

Fibril-containing SMC composites are prepared using conventional SMC processing equipment. This equipment,
15 which may be continuous belt or beltless, typically includes a mixing system, a paste metering system, a compaction system, and a take-up system.

The mixing system compounds the uncured resin (typically an unsaturated, thermosetting polyester or epoxy
20 resin which cures upon application of heat) and additives such as catalysts, fillers, thickeners, mold release agents, pigments, thermoplastic polymers (e.g., polyvinyl chloride polymers and copolymers and polyethylene powders for minimizing shrinkage during molding), flame retardants,
25 and ultraviolet absorbers into a paste having the consistency of pancake batter suitable for forming into a sheet. The paste also contains carbon fibrils. The mixing system may be of the batch, batch/continuous, or continuous type.

30 The paste is transported from the mixing system to a paste reservoir which, with the aid of adjustable doctor blades, meters a predetermined thickness of paste onto upper and lower plastic (e.g., polyethylene) carrier films.

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The height of the doctor blades determines the amount of resin paste in the final SMC composite. Between the two paste-covered sheets, reinforcing agents, e.g., chopped glass strand or continuous glass roving are applied to form a sandwich. Additional carbon fibrils may also be added at this stage. The total amount of carbon fibrils (i.e. the sum of the fibrils added during compounding of the paste plus any fibrils applied directly to the paste-covered sheets) preferably is between 1 and 4% by weight based upon resin.

A compactor compresses the sandwich to ensure that the resin paste wets the fibrils and any other reinforcement. Typically, the compactor consists of a series of serrated steel rollers or a dual wire mesh belt compaction module. The sheet exiting the compactor is then taken up, e.g., by a wind-up turret to form a roll. When a full roll of the composite is ready, the sheet (which typically is 2-5 feet wide) is cut and transferred to a second wind-up turret. The roll is then taped to prevent unwinding and a vapor barrier sleeve applied to prevent ultraviolet or moisture contamination. The roll is stored in a maturation room maintained at about 85-90°F for approximately 1-7 days to provide a uniform, reproducible viscosity for molding. The sheet is then cut and molded into the desired part using, e.g., compression or matched die molding.

The molded components thus prepared are useful in a variety of applications. In the automotive industry, they are useful as components of heating and ventilating systems, hoods, trunks, side panels, fenders, roof panels, front end panels incorporating fender extensions, mounts for headlamps and grilles, and cab components (e.g., hoods) for trucks. The molded composites are also useful as

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electrical switchgear housings, housings for hand power tools such as electric drills, and housings for appliances such as air conditioners and dishwashers. As in the case of the fibril-containing RIM composites, the parts can be electrostatically coated.

Example 3 - BMC

Fibril-containing BMC composites are prepared using conventional BMC processing equipment. Typically, this equipment consists of two mixers. The first mixer, e.g., a simple propeller type, or dissolver or disperser of the kind used in the paint industry, is used to mix the resin (e.g., unsaturated thermosetting polyester or epoxy resin as in the case of SMC composites) and additives such as particulate fillers, mold release agents, colorants, catalyst, thickeners, and low profile additives. The carbon fibrils also are preferably added to the resin mix. The components are well-mixed to disperse the additives and fibrils throughout the resin. The resulting mixture is then transferred to a second, heavy duty mixer, e.g., a dough mixer or double arm mixer, and additional reinforcing agents such glass fibers (in the form of chopped strand or chopped spun roving), asbestos, sisal, and organic fibers are added. An additional amount of carbon fibrils may also be added at this time. The total amount of carbon fibrils (i.e. the sum of the fibrils added during both mixing stages) is between 1 and 4% by weight based upon resin.

The second mixer mixes the components until the resulting mixture has the consistency of putty. The putty is then aged (e.g., for about 4 hours at 77°F). When aging is complete, the putty can be molded directly or stored in a sealed, refrigerated, plastic bag until needed. The putty can also be extruded in the form of bars or logs prior to aging to facilitate handling and storage.

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The fibril-reinforced BMC premix is molded using conventional thermoset molding techniques, e.g., compression, transfer, or thermoset injection molding at pressures sufficient to cause the premix to flow into the extremities of the mold; typical molding pressures range from about 100 - 1500 psi. The molded parts are useful in many of the same applications as SMC molded parts. Additional uses include automobile heater housings and related ducting. Like the RIM and SMC molded parts, the BMC molded parts can be electrostatically coating without prior application of an electrically conductive primer coat.

In addition to the above-described examples, fibrils can be incorporated into a wide variety of matrices (e.g., thermoplastic and thermoset matrices) in order to make the resulting composite sufficiently electrically conductive to permit direct electrostatic overcoating.

Conductive Coatings and Inks

A. Powder and Liquid Coatings

Both powder and liquid coatings consist of a polymeric binder into which carbon fibrils are incorporated. Preferred binders for the powder coatings include the following thermoset resins: urethane polyesters, epoxy, epoxy polyesters, polyester triglycidyl isocyanurates, and urethane or epoxy-type polyesters. Suitable thermoplastic resins include polyethylene, polypropylene, polyamide (e.g., nylon), polyvinyl chloride, and thermoplastic polyesters (e.g., polyethylene terephthalate). The molecular weight of the binder is sufficiently high such that it is a solid at room temperature. In the case of liquid coatings, preferred resins are thermoplastic polyesters and polyurethanes. The molecular weight of the

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binder is sufficiently low such that it is a liquid at room temperature.

Preferably, between 1 and 4% (by weight of resin) of carbon fibrils are incorporated into the binder to form an electrically conductive coating. Such loadings are sufficient to permit direct electrostatic overcoating of a dielectric part (e.g., a plastic) to which the coating is applied. The resistivities of these coatings following application typically are on the order of 10^6 ohm cm or less.

Preferred fibrils have small diameters (preferably between 3.5 and 75 nanometers), graphitic layers that are substantially parallel to the fibril axis, and are substantially free of a continuous thermal carbon overcoat, as described in Tennent, U.S. Pat. No. 4,663,230; Tennent et al.; U.S.S.N. 871,675; Tennent et al., U.S.S.N. 871,676; Snyder et al., U.S.S.N. 149,573; Mandeville et al., U.S.S.N. 285,817; and McCarthy et al., U.S.S.N. 351,967. These fibrils are prepared as described in the aforementioned patent and patent applications. The fibrils may also be treated to introduce oxygen-containing functional groups onto the fibril surface, as described in McCarthy et al., U.S.S.N. 351,967.

The coatings are prepared by combining the binder, fibrils, and additives such as pigments under shear mixing. Once the mixing is complete, the coatings are applied directly to a metal or molded plastic part or stored until needed.

The coatings are applied electrostatically in the mold to sheet molding compound (SMC) and bulk molding compound (BMC) compression molded parts such as automotive body panels. The coated part can then be used as is or

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electrostatically overcoated with a second coating, e.g., a finishing coat. In either case, the addition of the fibrils to the binder to render the coating electrically conductive makes direct electrostatic overcoating possible.

5

B. Inks

Preferred polymeric binders for the resistive and conductive inks are thermoset epoxy resins and thermoplastic polyester resins (e.g., polyethylene terephthalate). The inks may be provided in the form of solutions or solvent
10 dispersions.

Preferred fibrils are those described above in the case of the powder and liquid coatings. The amount of fibrils incorporated in the binder is a function of the desired resistivity level, which in turn is governed by the application for which the inks are intended. In general, for resistive inks having resistivities ranging from 10^{-2} to 10^6 ohm cm, from 1 to 30% by weight of fibrils are incorporated. In the case of conductive inks, which already have relatively low resistivities due to the
20 presence of e.g., silver flakes, the fibrils are used to fine tune the resistivity of the ink, making it possible to achieve resistivity values that are impractical or impossible to obtain simply by adjusting the amount of silver flakes; thus, the amount of fibrils incorporated
25 depends on the resistivity of the silver-filled binder and the targeted resistivity value. In general, between 20 and 50% by weight of fibrils are incorporated to lower the resistivity of silver-filled binders having resistivities greater than 1 ohm cm to a value less than 1 ohm cm.

30

The inks are prepared using the same procedures described above for the conductive powder and liquid coatings. They are then screen printed on a substrate such

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as a printed circuit board substrate or a disposable donor sheet for such a substrate to form electronic components such as resistors (in the case of resistive inks) or conductive traces for interconnecting electronic components (in the case of conductive inks) by conventional screen printing techniques. The consistent conductivity of the inks eliminates the need for laser trimming, allowing the inks to be used in multilayer molded circuit boards.

Elastomers

10 The composites are prepared by dispersing fibrils in an elastomer matrix. Preferred fibrils have small diameters (preferably between 3.5 and 75 nanometers), graphitic layers that are substantially parallel to the fibril axis, and are substantially free of a continuous thermal carbon overcoat, as described in Tennent, U.S. Pat. No. 4,663,230; Tennent et al.; U.S.S.N. 871,675; Tennent et al., U.S.S.N. 871,676; Snyder et al., U.S.S.N. 149,573; and Mandeville et al., U.S.S.N. 285,817. These fibrils are prepared as described in the aforementioned patent and patent applications. The fibrils may also be treated to introduce oxygen-containing functional groups onto the fibril surface, as described in McCarthy et al., U.S.S.N. 351,967. Preferred elastomer matrices include natural rubber, styrene-butadiene rubber (both random and block copolymers), polyisoprene, neoprene, chloroprene, polybutadiene (both cis and trans 1,4 and 1,2-polybutadienes), fluoroelastomers (e.g., fluorinated polyethylene), silicone rubbers, and urethane elastomers (e.g., Spandex).

30 Low fibril loadings are preferred. In general, between 1 and 10 parts of fibrils are added per 100 parts elastomer. Fillers such as carbon black and silica may

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also be added; preferably, four parts filler are used for every one part fibrils.

The particular compounding method used to prepare the fibril-filled elastomer composites depends on the the
5 end property sought, the type of elastomer matrix, the degree of dispersion required, and the type of fillers added in addition to the fibrils. For example, in rubber matrices such as natural rubber which have a significant measure of strength even in the absence of any separately
10 added reinforcing agents, conventional compounding equipment such as Banbury and two-roll mills can be used to prepare the composite. Where a high degree of uniform dispersion is desired, however, the fibrils are first broken up using techniques such as ball-milling. A
15 particularly effective method for achieving well-dispersed mixtures involves combining the fibrils, elastomer matrix, and any other fillers with a low viscosity additive (e.g., an oil or liquid solvent) and a milling promoter (e.g., abrasive particles) to form a slurry, and then agitating
20 that slurry at high speeds in, e.g., a stirred ball mill or attritor, as described in Creehan, U.S.S.N. _____, entitled "Preparation of Uniform Dispersions", filed concurrently with the present application and assigned to the same assignee as the present application which is
25 hereby incorporated by reference in its entirety. The viscosity modifier may also be built into the matrix, e.g., in the case of solution polymerized SBR. Once agitation is complete, any solvents can be removed by, e.g., vacuum drying, steam stripping, or freeze drying. The mixtures
30 can then be molded as is or subjected to further high shear compounding in, e.g., the Banbury or two-roll mill and then molded.

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During compounding, the amount of fibrils may be chosen so as to match the desired amount of fibrils in the final composite and added directly to the elastomer matrix. However, the fibril-filled composites may also be prepared by first combining a high (25 parts) amount of fibrils with the elastomer to form a masterbatch. An appropriate amount of the masterbatch designed to achieve the targeted amount of fibrils in the final composite (e.g., 5-10 parts) is then compounded with additional elastomer as described above to form the final composite.

The composites can be molded by application of heat or by resistive or inductive heating into a variety of articles using conventional elastomer molding techniques. Particularly useful articles include tires and tire components such as treads and casings, seals, and vibration damping agents. The uncured composites are useful as adhesives and bonding agents, e.g., as repair compounds for tires and conveyors. The adhesive can be cured in place by inductive or resistive heating. The physical properties of articles prepared from the fibril-filled elastomers (e.g., the air pressure of a tire) can be monitored electrically.

In addition to the above-described carbon fibrils, for example, fibrils having a crystalline graphitic structure and a morphology defined by a fishbone-like arrangement of the graphite layers along the fibril axis, as described in Geus et al., European Patent Application No. 0 198 558, published October 22, 1986, are also suitable. These fibrils are prepared by vapor phase deposition of hydrocarbon gas onto a monocrystalline metal particle catalyst (e.g., iron) having a diameter of at least 5 nm at temperatures between 250 and 800°C.

Friction Materials

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Preferred friction materials contain an organic resin binder into which carbon fibrils and other fillers are incorporated. The relative amounts of the ingredients depend on the particular application for which the friction material is intended. For example, for heavy duty applications such as brake shoes for large trucks where fade resistance and stopping power are critical, larger amounts of fibrils may be used compared to disc brake pads for automobiles. Typically, the amount of fibrils is up to 20% by weight of the composition based on resin.

The resin binder must be able to withstand the elevated temperatures encountered in use. Phenolic resins, because of their superior resistance to thermal degradation and relatively low cost, are preferred. Preferred fillers in addition to the fibrils include metal (e.g., brass) fibers, polyaramide fibers (e.g., Kevlar fibers available commercially from E.I. Du Pont de Nemours and Co.), mineral fillers such as diatomaceous earth and barium sulfate, graphite, and chopped carbon fibers. Incorporating the fibrils makes it possible to reduce the amounts of these additives relative to conventional friction material compositions.

Preferred fibrils have small diameters (preferably between 3.5 and 75 nanometers), graphitic layers that are substantially parallel to the fibril axis, and are substantially free of a continuous thermal carbon overcoat, as described in Tennent, U.S. Pat. No. 4,663,230; Tennent et al.; U.S.S.N. 871,675; Tennent et al., U.S.S.N. 871,676; Snyder et al., U.S.S.N. 149,573; and Mandeville et al., U.S.S.N. 285,817. These fibrils are prepared as described in the aforementioned patent and patent applications. The fibrils may also be treated to introduce oxygen-containing

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functional groups onto the fibril surface, as described in McCarthy et al., U.S.S.N. 351,967.

The friction materials are prepared by dry mixing the resin, fibrils, and other additives under shear, and then molding the resulting admixture at elevated temperatures using conventional thermoset molding techniques, e.g., compression or matched die molding. A friction material containing 8% by weight carbon fibrils (as described above) in a phenolic resin that also included metal fibers, diatomaceous earth, barium sulfate, Kevlar polyaramide fibers, graphite, and carbon fibers was prepared in the form of disc brake backing plates. The brakes exhibited improved friction at high temperature with lower fade (as measured by Dynamometer testing) compared to compositions lacking the fibrils. The brakes also exhibited improved resistance to cracking and spalling at high temperatures (750°F).

Hybrid Composites

Preferred hybrid composites are those in which the primary reinforcing agent consists of continuous or discontinuous fibers having mean diameters on the order of about 1 to 10 microns and the secondary reinforcing agent consists of carbon fibrils. Preferred fibrils have small diameters (preferably between 3.5 and 75 nanometers), graphitic layers that are substantially parallel to the fibril axis, and are substantially free of a continuous thermal carbon overcoat, as described in Tennent, U.S. Pat. No. 4,663,230; Tennent et al.; U.S.S.N. 871,675; Tennent et al., U.S.S.N. 871,676; Snyder et al., U.S.S.N. 149,573; and Mandeville et al., U.S.S.N. 285,817. These fibrils are prepared as described in the aforementioned patent and patent applications. The fibrils may also be treated to introduce oxygen-containing functional groups onto the

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fibril surface, as described in McCarthy et al., U.S.S.N. 351,967.

The composites may be unidirectional composites (i.e. composites in which the primary reinforcing agents are individual continuous fibers, all of which are arranged parallel to each other such that they reinforce the matrix primarily in one direction only), two-dimensional laminates or lay-ups of unidirectional tape or woven fabric (i.e. composites in which the primary reinforcing agents are continuous fibers that reinforce the matrix in more than one direction within a single plane), multi-dimensional laminates or lay-ups (i.e. composites in which reinforcement due to the continuous fibers is not confined to a single plane), and isotropic, discontinuous fiber-reinforced composites (i.e. composites in which primary reinforcement discontinuous fibers, e.g., chopped glass or carbon fibers, or carbon whiskers, are randomly oriented throughout the matrix to provide uniform reinforcement). Thermoset resins are preferred where the primary reinforcing agents are continuous fibers, while both thermoplastic and thermoset resins are suitable in the case of discontinuous fibers.

The Figure shows a two-dimensional woven laminate 10 in which an epoxy matrix 12 is reinforced with layers of primary reinforcing fibers 14 and carbon fibrils 16. Primary fibers 12 are polyacrylonitrile - based carbon fibers. Each layer of primary fibers is woven to reinforce epoxy matrix 12 in two mutually perpendicular directions within a single plane. Carbon fibrils 16 are uniformly dispersed throughout matrix 12 and randomly oriented with respect to primary fibers 14.

The composites are prepared by dispersing the fibrils throughout the resin (which is in the form of a viscous liquid, paste, or melt to facilitate mixing) to

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form a prepreg. A particularly effective method for achieving well-dispersed prepreps in which the majority of fibril agglomerates have mean diameters less than $0.5\mu\text{m}$ involves combining the fibrils, matrix, and any other fillers with a low viscosity additive (e.g., an oil or liquid solvent) and a milling promoter (e.g., abrasive particles such as grit particles) to form a slurry, and then agitating that slurry at high speeds in, e.g., a stirred ball mill or attritor, as described in Creehan, U.S.S.N. _____, entitled "Preparation of Uniform Dispersions", filed concurrently with the present application and assigned to the same assignee as the present application which is hereby incorporated by reference in its entirety. Once agitation is complete, any solvents can be removed by, e.g., vacuum drying, steam stripping, or freeze drying. If the primary reinforcing agents are discontinuous fibers, they can be added to the resin along with the fibrils. If the primary reinforcing agents are continuous fibers, the resin-fibril mixture is applied to the primary reinforcing agents using conventional impregnation techniques, taking care to ensure that the resin-fibril mixture adequately wets the primary reinforcing agents. The composite is then molded and cured using conventional molding methods. The composite shown in the Figure was prepared as follows.

An uncured epoxy resin consisting of 9 parts N,N,N',N'-tetraglycidyl-4,4'-methylene bisbenzenamine (commercially available from Ciba Geigy as MY720 epoxy), 1 part Bisphenol-A with epichlorohydrin (commercially available from Ciba Geigy as GY6010 epoxy), and 5 parts 4,4'-diaminodiphenyl sulfone hardener (commercially available from Ciba Geigy as HT976 hardener) was combined with a volume of carbon fibrils (prepared as described in

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the aforementioned Snyder et al. application) using a stirred ball mill until the fibrils were uniformly dispersed throughout the resin (as described in the aforementioned Creehan application); the fibril volume fraction of the samples prepared varied from 0.01 to 0.05 based on total resin content. The mixture was then applied by hand to a six ply laminate of woven polyacrylonitrile-based carbon fiber fabric (Techniweave 8 Harness Satin Weave 8HS style 3K-175-8H of Celion 3K yarn having a yarn count of 24 x 23 (± 1) and an areal density of 10.7 oz./yd² (± 1)). The composite fabric volume fraction was 0.60 ± 0.02 . The resulting composite was then molded and cured to form the final composite structure. The properties of a composite in which the fibril volume fraction was 0.025 were measured and compared to a control sample containing no fibrils. The results demonstrated that the randomly oriented, uniformly dispersed fibrils improve matrix-dominated properties such as compressive strength, short beam shear strength, in-plane shear strength, and trans-ply resistivity, and properties such as flexural strength and modulus which have a significant matrix component, without interfering with properties such as tensile strength and modulus which are dominated by the continuous fibers.

Other embodiments are within the following claims.

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Claims

- 1 1. A composite comprising a reaction injection
2 molded matrix into which carbon fibrils have been
3 incorporated.
- 1 2. A composite comprising the molded product of a
2 premix that includes a resin matrix into which carbon
3 fibrils have been incorporated.
- 1 3. The composite of claim 2 wherein said premix is
2 a sheet molding compound.
- 1 4. The composite of claim 2 wherein said premix is
2 a bulk molding compound.
- 1 5. The composite of claim 1 or 2 wherein the
2 amount of said fibrils is sufficient to impart to said
3 composite an electrical conductivity sufficiently high to
4 permit direct electrostatic overcoating.
- 1 6. The composite of claim 1 or 2 wherein the
2 electrical conductivity of said composite is greater than
3 the electrical conductivity of a composite in which the
4 same matrix is filled with an equivalent amount of carbon
5 black.
- 1 7. The composite of claim 1 or 2 wherein the
2 amount of said fibrils is less than or equal to 20% by
3 weight.
- 1 8. The composite of claim 7 wherein the amount of
2 said fibrils is less than or equal to 4% by weight.

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1 9. The composite of claim 1 or 2 wherein the
2 amount of said fibrils is less than or equal to 4% by
3 weight and is sufficient to impart to said composite an
4 electrical conductivity sufficiently high to permit direct
5 electrostatic overcoating.

1 10. The composite of claim 1 or 2 wherein the
2 amount of said fibrils is sufficient to impart to said
3 composite an electrical conductivity sufficiently high to
4 dissipate static electricity.

1 11. The composite of claim 1 or 2 wherein the
2 amount of said fibrils is less than or equal to 4% by
3 weight and is sufficient to impart to said composite an
4 electrical conductivity sufficiently high to dissipate
5 static electricity.

1 12. The composite of claim 1 or 2 wherein said
2 fibrils comprise tubes having graphitic layers that are
3 substantially parallel to the fibril axis.

1 13. The composite of claim 12 wherein the length
2 to diameter ratio of said fibrils is at least 5.

1 14. The composite of claim 12 wherein the diameter
2 of said fibrils is between 3.5 and 75 nanometers,
3 inclusive.

1 15. The composite of claim 12 wherein said fibrils
2 are substantially free of a continuous thermal carbon
3 overcoat.

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1 16. The composite of claim 12 wherein the outer
2 surface of said graphitic layers has bonded thereto a
3 plurality of oxygen-containing groups, or derivatives
4 thereof.

1 17. The composite of claim 1 or 2 wherein said
2 matrix comprises a thermoplastic material.

1 18. The composite of claim 17 wherein said matrix
2 comprises a polyamide, polyurethane, polyurea, or an
3 elastomer, or a mixture thereof.

1 19. The composite of claim 1 or 2 wherein said
2 matrix comprises a thermoset material.

1 20. The composite of claim 19 wherein said matrix
2 comprises a polydicyclopentadiene, polyester, thermosetting
3 polyurethane, vinylacrylimide, or epoxy resin, or a mixture
4 thereof.

1 21. The composite of claim 1 or 2 wherein said
2 composite is molded in the form of an automotive part.

1 22. A composite in a form suitable for reaction
2 injection molding comprising one or more liquid reactants
3 capable of polymerizing to form a reaction injection molded
4 matrix and carbon fibrils.

1 23. A premix comprising a resin into which carbon
2 fibrils are incorporated.

1 24. The premix of claim 23 wherein said premix is
2 in the form of a sheet molding compound.

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1 25. The premix of claim 23 wherein said premix is
2 in the form of a bulk molding compound.

1 26. The composition of claim 22 or 23 wherein the
2 amount of said fibrils is less than or equal to 20% by
3 weight.

1 27. The composition of claim 26 wherein the amount
2 of said fibrils is less than or equal to 4% by weight.

1 28. The composition of claim 22 or 23 wherein said
2 fibrils comprise tubes having graphitic layers that are
3 substantially parallel to the fibril axis.

1 29. The composition of claim 28 wherein the length
2 to diameter ratio of said fibrils is at least 5.

1 30. The composition of claim 28 wherein the
2 diameter of said fibrils is between 3.5 and 75 nanometers,
3 inclusive.

1 31. The composition of claim 28 wherein said
2 fibrils are substantially free of a continuous thermal
3 carbon overcoat.

1 32. The composition of claim 28 wherein the outer
2 surface of said graphitic layers has bonded thereto a
3 plurality of oxygen-containing groups, or derivatives
4 thereof.

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1 33. The composition of claim 22 wherein said
2 liquid reactants comprise one or more polyols,
3 polyisocyanates, or polyamines.

1 34. The composition of claim 23 wherein said resin
2 comprises a thermosetting resin.

1 35. A method of preparing a composite that includes
2 a reaction injection molded matrix into which carbon
3 fibrils have been incorporated comprising the steps of
4 mixing said fibrils with one or more liquid
5 reactants capable of polymerizing to form said matrix;
6 introducing the mixture into a mold; and
7 molding the mixture under reaction conditions
8 including pressure and temperature to prepare said
9 composite in the form of a molded part.

1 36. A method of preparing a composite that
2 includes a sheet molding compound into which carbon fibrils
3 have been incorporated comprising the steps of
4 mixing said fibrils with a resin; and
5 forming the mixture into a sheet.

1 37. The method of claim 36 further comprising
2 molding said composite under reaction conditions including
3 pressure and temperature to prepare said composite in the
4 form of a molded part.

1 38. A method of preparing a composite that
2 includes a bulk molding compound into which carbon fibrils
3 have been incorporated comprising mixing said fibrils with
4 a resin to form a putty suitable for molding.

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1 39. The method of claim 38 further comprising
2 molding said composite under reaction conditions including
3 pressure and temperature to prepare said composite in the
4 form of a molded part.

1 40. The method of claim 35, 37, or 39 further
2 comprising directly electrostatically overcoating said
3 molded part.

1 41. A composite prepared according to the method of
2 claim 35, 36, 37, 38, or 39.

1 42. A composite comprising a matrix into which
2 carbon fibrils are incorporated, the amount of said fibrils
3 being sufficient to permit said composite to be directly
4 electrostatically overcoated.

1
2 43. A compounding process for preparing a
3 composite comprising the steps of
4 introducing one or more fillers and a matrix
5 material into a stirred ball mill; and
6 subjecting said fillers and said matrix material to
7 a combination of shear and impact forces under reaction
8 conditions including reaction time sufficient to reduce the
9 size of agglomerates formed by said fillers to a value
10 below a pre-determined value to disperse said fillers
11 throughout said matrix material.

1 44. The compounding process of claim 43 wherein
2 said pre-determined value of said agglomerate size is no
3 greater than 1000 times the size of said filler.

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1 45. The compounding process of claim 44 wherein
2 said pre-determined value of said agglomerate size is no
3 greater than 100 times the size of said filler.

1 46. The compounding process of claim 45 wherein
2 said pre-determined value of said agglomerate size is no
3 greater than 10 times the size of said filler.

1 47. The compounding process of claim 44, 45, or 46
2 wherein one or more of the characteristic dimensions of
3 said filler is less than 1 μm .

1 48. The compounding process of claim 47 wherein
2 one or more of the characteristic dimensions of said filler
3 is less than 0.1 μm .

1 49. The compounding process of claim 43 further
2 comprising adding a viscosity modifier to said stirred ball
3 mill.

1 50. The compounding process of claim 49 wherein
2 said viscosity modifier is removed following the dispersion
3 step.

1 51. The compounding process of claim 50 wherein
2 said viscosity modifier is a solvent.

1 52. The compounding process of claim 49 wherein
2 said viscosity modifier is retained following the dispersion
3 step.

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1 53. The compounding process of claim 52 wherein
2 said viscosity modifier is a reactive diluent that
3 chemically reacts with said matrix material.

1 54. The compounding process of claim 43 further
2 comprising adding one or more milling media to said stirred
3 ball mill.

1 55. The compounding process of claim 43 wherein
2 said filler comprises whiskers.

1 56. The compounding process of claim 43 wherein
2 said filler comprises discontinuous fibers.

1 57. The compounding process of claim 43 wherein
2 said filler comprises a particulate filler.

1 58. The compounding process of claim 43 wherein
2 said filler comprises carbon fibrils.

1 59. The composite of claim 58 wherein said fibrils
2 comprise tubes having graphitic layers that are
3 substantially parallel to the fibril axis.

1 60. The composite of claim 58 wherein the length
2 to diameter ratio of said fibrils is at least 5.

1 61. The composite of claim 58 wherein the diameter
2 of said fibrils is between 3.5 and 75 nanometers,
3 inclusive.

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1 62. The composite of claim 58 wherein said fibrils
2 are substantially free of a continuous thermal carbon
3 overcoat.

1 63. The composite of claim 58 wherein the outer
2 surface of said graphitic layers has bonded thereto a
3 plurality of oxygen-containing groups, or derivatives
4 thereof.

1 64. The composite of claim 43 wherein said matrix
2 material comprises a metal powder.

1 65. The composite of claim 43 wherein said matrix
2 material comprises a ceramic powder.

1 66. The composite of claim 65 wherein said ceramic
2 powder comprises a glass powder.

1 67. The composite of claim 43 wherein said matrix
2 material comprises a thermoplastic resin.

1 68. The composite of claim 67 wherein said
2 thermoplastic resin is a thermoplastic polyester,
3 polyurethane, polyether ether ketone, polyether sulfone,
4 polyether imide, polyamide, or polyurea resin.

1 69. The compounding process of claim 43 wherein
2 said matrix material comprises a thermoset resin.

1 70. The compounding process of claim 69 wherein
2 said thermoset resin is a phenolic, epoxy, thermosetting
3 polyurethane, thermosetting polyester, polyimide,

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4 bismaleimide, polycyclopentadiene, or vinylacrylimide
5 resin.

1 71. The compounding process of claim 43 wherein
2 said matrix material comprises an elastomer.

1 72. The compounding process of claim 71 wherein
2 said elastomer is styrene-butadiene rubber, natural rubber,
3 ethylene-propylene-diene monomer rubber, silicone rubber,
4 polybutadiene, polyisoprene, neoprene, chloroprene,
5 fluoroelastomer, or a urethane elastomer.

1 73. The compounding process of claim 43 wherein
2 said matrix material is in the form of a liquid.

1 74. The compounding process of claim 43 wherein
2 said matrix material is a thermoplastic resin, said process
3 further comprising cooling the contents of said stirred
4 ball mill to a temperature at which said matrix material
5 becomes brittle and maintaining said temperature throughout
6 the dispersion step.

1 75. The compounding process of claim 43 wherein
2 said matrix material is a thermoplastic or thermoset resin,
3 said filler comprises carbon fibrils, and a viscosity
4 modifier and milling media are added to said stirred ball
5 mill.

1 76. A composite prepared according to the method
2 of claim 43.

1
2 77. A hybrid composite comprising a matrix into
3 which is incorporated a primary fibrous reinforcing agent

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4 and a secondary reinforcing agent uniformly dispersed
5 throughout said matrix and randomly oriented relative to
6 said primary reinforcing agent.

1 78. The composite of claim 77 wherein the mean
2 diameter of said primary reinforcing agent is at least 10
3 times greater than the mean diameter of said secondary
4 reinforcing agent.

1 79. The composite of claim 78 wherein the mean
2 diameter of said primary reinforcing agent is at least 100
3 times greater than the mean diameter of said secondary
4 reinforcing agent.

1 80. A hybrid composite comprising a matrix into
2 which is incorporated a primary fibrous reinforcing agent
3 and a secondary fibrous reinforcing agent, said primary
4 reinforcing agent having a mean diameter that is at least
5 1000 times greater than the mean diameter of said secondary
6 reinforcing agent.

1 81. The hybrid composite of claim 80 wherein said
2 secondary reinforcing agent is dispersed uniformly
3 throughout said matrix and randomly oriented relative to
4 said primary reinforcing agent.

1 82. The composite of claim 77 or 80 wherein the
2 majority of agglomerates formed by said secondary
3 reinforcing agent in said matrix are no greater than 10 μ m.

1 83. The composite of claim 82 wherein the majority
2 of said agglomerates are no greater than 0.5 μ m.

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1 84. The composite of claim 77 wherein said
2 secondary reinforcing agent comprises carbon microfibers.

1 85. The composite of claim 77 wherein said
2 secondary reinforcing agent comprises whiskers.

1 86. The composite of claim 77 wherein said
2 secondary reinforcing agent comprises chopped fibers.

1 87. The composite of claim 77 wherein said
2 secondary reinforcing agent comprises a particulate
3 reinforcing agent.

1 88. The composite of claim 77 or 80 wherein said
2 secondary reinforcing agent comprises carbon fibrils.

1 89. The composite of claim 88 wherein said carbon
2 fibrils comprise tubes having graphitic layers that are
3 substantially parallel to the fibril axis.

1 90. The composite of claim 88 wherein the length
2 to diameter ratio of said fibrils is at least 5.

1 91. The composite of claim 88 wherein the diameter
2 of said fibrils is between 3.5 and 75 nanometers,
3 inclusive.

1 92. The composite of claim 88 wherein said fibrils
2 are substantially free of a continuous thermal carbon
3 overcoat.

1 93. The composite of claim 77 or 80 wherein said
2 primary reinforcing agent comprises continuous fibers.

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1 94. The composite of claim 93 wherein said
2 continuous fibers comprise carbon, glass, ceramic, or
3 polyaramide fibers.

1 95. The composite of claim 93 wherein said said
2 continuous fibers are woven, knit, crimped, or straight.

1 96. The composite of claim 77 or 80 wherein said
2 primary reinforcing agent comprises discontinuous fibers.

1 97. The composite of claim 77 or 80 wherein said
2 matrix comprises an organic thermoset resin.

1 98. The composite of claim 97 wherein said
2 thermoset resin is an epoxy, bismaleimide, polyimide, or
3 polyester resin.

1 99. The composite of claim 77 or 80 wherein said
2 matrix comprises an organic thermoplastic resin.

1 100. The composite of claim 99 wherein said
2 thermoplastic resin is a polyethylene, oriented
3 polyethylene, polypropylene, polyamide, polyurethane,
4 polyvinyl chloride, thermoplastic polyester resin,
5 polyether ether ketone, polyether sulfone, polyether imide,
6 liquid crystalline polymer, or reaction injection molded
7 resin.

1 101. The composite of claim 77 or 80 wherein said
2 matrix comprises an inorganic polymer.

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1 102. The composite of claim 77 or 80 wherein said
2 matrix comprises a metal.

1 103. The composite of claim 77 or 80 wherein said
2 matrix comprises a ceramic material.

1 104. The composite of claim 77 or 80 wherein said
2 matrix is carbon.

1 105. The composite of claim 77 or 80 wherein the
2 amount of said secondary reinforcing agent incorporated in
3 said matrix is less than or equal to 20% by volume.

1 106. The composite of claim 105 wherein the amount
2 of said secondary reinforcing agent incorporated in said
3 matrix is between 1 and 10% by volume.

1 107. The composite of claim 77 or 80 wherein said
2 secondary reinforcing agent comprises carbon fibrils that
3 are tubes having graphitic layers that are substantially
4 parallel to the fibril axis, a length to diameter ratio of
5 at least 5, a diameter between 3.5 and 75 nanometers,
6 inclusive, and which are substantially free of a continuous
7 thermal carbon overcoat; and said primary reinforcing agent
8 comprises continuous carbon fibers.

1 108. A process for preparing a hybrid composite
2 comprising combining a matrix with a fibrous primary
3 reinforcing agent and a secondary reinforcing agent such
4 that said secondary reinforcing agent is uniformly
5 dispersed throughout said matrix and randomly oriented
6 relative to said primary reinforcing agent.

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1 109. A process for preparing a hybrid composite
2 comprising combining a matrix with a fibrous secondary
3 reinforcing agent and a fibrous primary reinforcing agent
4 having a mean diameter at least 100 times greater than the
5 mean diameter of said secondary reinforcing agent.

1 110. The process of claim 109 wherein said primary
2 reinforcing agent and said secondary reinforcing agent are
3 combined with said matrix in such a way that said secondary
4 reinforcing agent is dispersed uniformly throughout said
5 matrix and randomly oriented relative to said primary
6 reinforcing agent.

1 111. The process of claim 108 or 109 wherein said
2 microfibers are carbon fibrils.

1 112. A brake, or component thereof, comprising a
2 friction material that includes a matrix into which carbon
3 fibrils have been incorporated.

1 113. A clutch, or component thereof, comprising a
2 friction material that includes a matrix into which carbon
3 fibrils have been incorporated.

1 114. An automatic transmission disk, or component
2 thereof, comprising a friction material that includes a
3 matrix into which carbon fibrils have been incorporated.

1 115. The article of claim 112, 113, or 114 wherein
2 the amount of said fibrils is less than or equal to 20% by
3 weight.

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1 116. The article of claim 115 wherein the amount
2 of said fibrils is between 5 and 10% by weight.

1 117. The article of claim 112, 113, or 114 wherein
2 said fibrils comprise tubes having graphitic layers that
3 are substantially parallel to the fibril axis.

1 118. The article of claim 117 wherein the length
2 to diameter ratio of said fibrils is at least 5.

1 119. The article of claim 117 wherein the diameter
2 of said fibrils is between 3.5 and 75 nanometers, inclusive.

1 120. The article of claim 117 wherein said fibrils
2 are substantially free of a continuous thermal carbon
3 overcoat.

1 121. The article of claim 117 wherein the outer
2 surface of said graphitic layers has bonded thereto a
3 plurality of oxygen-containing groups, or derivatives
4 thereof.

1 122. The article of claim 112, 113, or 114 wherein
2 said matrix comprises a thermoset resin.

1 123. The article of claim 122 wherein said matrix
2 comprises a phenolic, polyester, or epoxy resin.

1 124. The article of claim 112, 113, or 114 wherein
2 said matrix comprises carbon.

1 125. The article of claim 112, 113, or 114 further
2 comprising one or more fillers.

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1 126. The article of claim 125 wherein said fillers
2 are metal, glass, ceramic, carbon, or polyaramide fibers.

1 127. The article of claim 125 wherein said fillers
2 are particulate fillers.

1 128. The article of claim 125 wherein said fillers
2 comprise one or more of graphite, clay, barium sulfate,
3 diatomaceous earth, silica, magnesia, beryllia, alumina,
4 silicon carbide, titanium dioxide, or carbon black.

1 129. A composite in the form of a friction material
2 comprising a matrix into which carbon fibrils have been
3 incorporated.

1 130. The composite of claim 129 wherein said
2 fibrils comprise tubes having graphitic layers that are
3 substantially parallel to the fibril axis, a length to
4 diameter ratio of said fibrils is at least 5, a diameter
5 between 3.5 and 75 nanometers, inclusive, and which are
6 substantially free of a continuous thermal carbon overcoat.

1 131. An electrically conductive composite in a form
2 suitable for applying to the surface of a substrate, said
3 composite comprising a polymeric binder into which carbon
4 fibrils are incorporated.

1 132. The composite of claim 131 wherein said
2 composite is in the form of a powder coating.

1 133. The composite of claim 131 wherein said
2 composite is in the form of a liquid coating.

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1 134. The coating of claim 132 or 133 wherein the
2 amount of said fibrils is sufficiently high to permit a
3 substrate to which said coating has been applied to be
4 electrostatically overcoated directly.

1 135. The coating of claim 132 or 133 wherein the
2 amount of said fibrils is less than or equal to 15% by
3 weight.

1 136. The coating of claim 135 wherein the amount
2 of said fibrils is between 0.5 and 10% by weight.

1 137. The coating of claim 136 wherein the amount
2 of said fibrils is between 1 and 4% by weight.

1 138. The coating of claim 132 or 133 wherein the
2 amount of said fibrils is less than or equal to 15% by
3 weight and is sufficient to permit a substrate to which
4 said coating has been applied to be electrostatically
5 overcoated directly.

1 139. The composite of claim 131 wherein said
2 composite is in the form of a resistive ink suitable for
3 screen printing on the surface of a substrate to form an
4 electronic component.

1 140. The resistive ink of claim 139 wherein the
2 amount of said fibrils is sufficient to decrease the bulk
3 resistivity of said binder to a value between 10^{-2} and 10^6
4 ohm cm when applied to a substrate.

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1 141. The resistive ink of claim 140 wherein said
2 resistivity is between 10^{-1} and 10^4 ohm cm.

1 142. The resistive ink of claim 139 wherein the
2 amount of said fibrils is between 1 and 30% by weight.

1 143. The resistive ink of claim 139 wherein the
2 amount of said fibrils is between 1 and 30% by weight and is
3 sufficient to decrease the bulk resistivity of said binder
4 to a value between 10^{-2} and 10^6 ohm cm when applied to a
5 substrate.

1 144. The composite of claim 131 wherein said
2 composite further comprises electrically conductive
3 graphite or metal particles and is in the form of a
4 conductive ink suitable for printing on the surface of a
5 substrate,

6 the amount of said fibrils being sufficient to
7 decrease the bulk resistivity of the particle-filled binder
8 by a predetermined amount when applied to a substrate.

1 145. The conductive ink of claim 144 wherein the
2 bulk resistivity of said particle-filled binder is greater
3 than 1 ohm cm and the amount of said fibrils is sufficient
4 to reduce the bulk resistivity to less than 1 ohm cm.

1 146. The conductive ink of claim 144 wherein the
2 bulk resistivity of said particle-filled binder is greater
3 than 10^{-1} ohm cm and the amount of said fibrils is
4 sufficient to reduce the bulk resistivity to less than 10^{-1}
5 ohm cm.

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1 147. The conductive ink of claim 144 wherein the
2 amount of said fibrils is less than or equal to 30% by
3 weight.

1 148. The conductive ink of claim 144 wherein the
2 bulk resistivity of said particle-filled binder is greater
3 than 1 ohm cm, and the amount of said fibrils is less than
4 or equal to 30% by weight and is sufficient to reduce the
5 bulk resistivity to less than 1 ohm cm.

1 149. The conductive ink of claim 144 wherein said
2 metal particles comprise silver flakes.

1 150. The composite of claim 131 wherein said
2 fibrils comprise tubes having graphitic layers that are
3 substantially parallel to the fibril axis.

1 151. The composite of claim 150 wherein the length
2 to diameter ratio of said fibrils is at least 5.

1 152. The composite of claim 150 wherein the
2 diameter of said fibrils is between 3.5 and 75 nanometers,
3 inclusive.

1 153. The composite of claim 150 wherein said
2 fibrils are substantially free of a continuous thermal
3 carbon overcoat.

1 154. The composite of claim 131 wherein said binder
2 comprises a thermoplastic resin.

1 155. The composite of claim 154 wherein said binder
2 comprises a polyethylene, polypropylene, polyamide,

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3 polyurethane, polyvinyl chloride, or thermoplastic
4 polyester resin.

1 156. The composite of claim 131 wherein said
2 binder comprises a thermoset resin.

1 157. The composite of claim 156 wherein said
2 binder comprises a saturated polyester, alkyd, or epoxy
3 resin.

1 158. The coating of claim 132 or 133 further
2 comprising at least one pigment.

1 159. A substrate coated with an electrically
2 conductive composite comprising a polymeric binder into
3 which carbon fibrils are incorporated.

1 160. The substrate of claim 159 wherein the
2 conductivity of said composite is sufficiently high to
3 permit said substrate to be electrostatically overcoated
4 directly.

1 161. The substrate of claim 159 wherein said
2 substrate comprises a substrate for a printed circuit board
3 and said composite is a resistive ink printed on said
4 substrate in the form of an electronic component.

1 162. The substrate of claim 161 wherein said
2 electronic component is a resistor.

1 163. The substrate of claim 159 wherein said
2 substrate comprises a substrate for a printed circuit board
3 and said composite is a conductive ink printed on said

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4 substrate in the form of a conductive trace for electrically
5 connecting electronic components.

1 164. A method for coating a substrate comprising
2 the steps of
3 preparing an electrically conductive coating by
4 incorporating carbon fibrils into a polymeric binder; and
5 applying said coating to said substrate.

1 165. The method of claim 164 further comprising
2 electrostatically applying an overcoating directly to the
3 coated substrate.

1 166. A method for printing on a substrate
2 comprising the steps of
3 preparing an ink by incorporating carbon fibrils in
4 a polymeric binder; and
5 screen printing said ink on said substrate.

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1 167. A composite comprising an elastomer matrix
2 into which carbon fibrils are incorporated,
3 said fibrils being characterized as having a
4 morphology consisting of tubes that are free of a continuous
5 thermal carbon overcoat and have graphitic layers that are
6 substantially parallel to the fibril axis.

1 168. The composite of claim 167 wherein the
2 diameter of said fibrils is less than 100 nanometers.

1 169. The composite of claim 168 wherein the
2 diameter of said fibrils is between 3.5 and 75 nanometers,
3 inclusive.

1 170. The composite of claim 167 wherein the length
2 to diameter ratio of said fibrils is between 5 and 100.

1 171. A composite comprising an elastomeric matrix
2 into which carbon fibrils are incorporated,
3 said fibrils being characterized as having a
4 crystalline graphitic structure and a morphology defined by
5 a fishbone-like arrangement of the graphite layers along the
6 fibril axis.

1 172. The composite of claim 171 wherein the
2 diameter of said fibrils is less than 100 nanometers.

1 173. The composite of claim 167 or 171 wherein said
2 elastomer matrix is selected from the group consisting of
3 natural rubber, styrene-butadiene rubber, polyisoprene,
4 neoprene, chloroprene, polybutadiene, fluoroelastomers,
5 silicone rubbers, and urethane elastomers.

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1 174. The composite of claim 167 or 171 further
2 comprising at least one filler.

1 175. The composite of claim 174 wherein said
2 filler is carbon black, silica, or a combination thereof.

1 176. The composite of claim 174 wherein the ratio
2 of the amount of said fibrils to the total amount of said
3 fillers is at least 1:4.

1 177. The composite of claim 167 or 171 wherein the
2 amount of fibrils in said composite is less than 25 parts
3 per 100 parts of elastomer.

1 178. The composite of claim 177 wherein the amount
2 of fibrils in said composite is less than 10 parts per 100
3 parts of elastomer.

1 179. The composite of claim 178 wherein the amount
2 of fibrils in said composite is greater than 25 parts per
3 100 parts of elastomer.

1 180. The composite of claim 167 or 171 wherein the
2 amount of fibrils in said composite is sufficiently high to
3 permit curing of said composite by resistive or inductive
4 heating.

1 181. The composite of claim 167 or 171 wherein the
2 amount of fibrils in said composite is less than 25 parts
3 per 100 parts of elastomer and is sufficient to permit
4 curing of said composite by resistive or inductive heating.

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1 182. The composite of claim 167 or 171 wherein the
2 amount of fibrils in said composite is sufficiently high to
3 permit at least one of the physical properties of said
4 composite to be monitored electrically.

1 183. The composite of claim 167 or 171 wherein the
2 amount of fibrils in said composite is less than 25 parts
3 per 100 parts of elastomer and is sufficient to permit at
4 least one of the physical properties of said composite to
5 be monitored electrically.

1 184. The composite of claim 167 or 171 wherein said
2 composite is in the form of an elastomer solution.

1 185. The composite of claim 167 or 171 wherein said
2 composite is in the form of a tire or component thereof.

1 186. The composite of claim 167 or 171 wherein said
2 composite is in the form of a seal.

1 187. The composite of claim 167 or 171 wherein said
2 composite is in the form of an adhesive.

1 188. A method for curing an elastomer comprising
2 the steps of
3 preparing a composite by incorporating carbon
4 fibrils in an elastomer matrix, the amount of said fibrils
5 being sufficient to impart to said composite an electrical
6 conductivity sufficiently high to permit resistive or
7 inductive heating; and
8 heating said composite resistively or inductively
9 to effect cure.

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1 189. A method for monitoring the physical condition
2 of an elastomer comprising the steps of
3 preparing a composite by incorporating an
4 lectrically conductive additive in an elastomer matrix, the
5 amount of said additive being sufficient to impart to said
6 composite an electrical conductivity sufficiently high to
7 permit the physical condition of said elastomer to be
8 monitored electrically; and
9 monitoring the electrical properties of said
10 composite as an indication of the physical condition of
11 said elastomer.

1 190. The method of claim 189 wherein said
2 electrically conductive additive comprises carbon fibrils.

1 191. The method of claim 189 or 190 wherein said
2 elastomer is in the form of a tire and the pressure in said
3 tire is monitored.

1 192. The method of claim 189 or 190 wherein said
2 elastomer is monitored for the presence of rips, tears, or
3 perforations.

1 193. The method of claim 188 or 190 wherein the
2 amount of fibrils is less than 25 parts per 100 parts of
3 elastomer.

1 194. The method of claim 193 wherein the amount of
2 fibrils is less than 10 parts per 100 parts of elastomer.

1 195. The method of claim 188 or 190 wherein said
2 fibrils are characterized as having a morphology consisting

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3 of tubes having graphitic layers that are substantially
4 parallel to the fibril axis.

1 196. The composite of claim 195 wherein the length
2 to diameter ratio of said fibrils is between 5 and 100.

1 197. The composite of claim 195 wherein the
2 diameter of said fibrils is between 3.5 and 75 nanometers,
3 inclusive.

1 198. The composite of claim 195 wherein said
2 fibrils are substantially free of a continuous thermal
3 carbon overcoat.

1 199. The composite of claim 188 or 190 wherein
2 said fibrils are characterized as having a crystalline
3 graphitic structure and a morphology defined by a
4 fishbone-like arrangement of the graphite layers along the
5 fibril axis.

1 200. A method for preparing an elastomer composite
2 comprising the steps of

3 preparing a masterbatch by dispersing in an
4 elastomer at least 25 parts of fibrils per 100 parts of
5 elastomer; and

6 compounding a predetermined portion of said
7 masterbatch with an additional amount of an elastomer to
8 prepare said composite.

1 201. The method of claim 200 wherein the amount of
2 fibrils in said composite is less than 25 parts per 100
3 parts of elastomer.

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1 202. The method of claim 201 wherein the amount of
2 fibrils in said composite is less than 10 parts per 100
3 parts of elastomer.

1 203. The method of claim 200 wherein said fibrils
2 are characterized as having a morphology consisting of
3 tubes having graphitic layers that are substantially
4 parallel to the fibril axis.

1 204. The composite of claim 203 wherein the length
2 to diameter ratio of said fibrils is between 5 and 100.

1 205. The composite of claim 203 wherein the
2 diameter of said fibrils is between 3.5 and 75 nanometers,
3 inclusive.

1 206. The composite of claim 203 wherein said
2 fibrils are substantially free of a continuous thermal
3 carbon overcoat.

1 207. The composite of claim 200 wherein said
2 fibrils are characterized as having a crystalline graphitic
3 structure and a morphology defined by a fishbone-like
4 arrangement of the graphite layers along the fibril axis.

1 208. The method of claim 200 furthering comprising
2 incorporating carbon black into said composite.

1 209. A method of reinforcing an elastomer
2 comprising incorporating into an elastomer matrix an amount
3 of carbon fibrils sufficient to enhance the mechanical
4 properties of said elastomer,

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5 said fibrils being characterized as having a
6 morphology consisting of tubes that are free of a continuous
7 thermal carbon overcoat and have graphitic layers that are
8 substantially parallel to the fibril axis.

1 210. The method of claim 209 wherein the diameter
2 of said fibrils is less than 100 nanometers.

1 211. The method of claim 210 wherein the diameter
2 of said fibrils is between 3.5 and 75 nanometers, inclusive.

1 212. The method of claim 209 wherein the length to
2 diameter ratio of said fibrils is between 5 and 100.

1 213. A method of reinforcing an elastomer
2 comprising incorporating into an elastomer matrix an amount
3 of carbon fibrils sufficient to enhance the mechanical
4 properties of said elastomer,

5 said fibrils being characterized as having a
6 crystalline graphitic structure and a morphology defined by
7 a fishbone-like arrangement of the graphite layers along
8 the fibril axis.

1 214. The method of claim 213 wherein the diameter
2 of said fibrils is less than 100 nanometers.

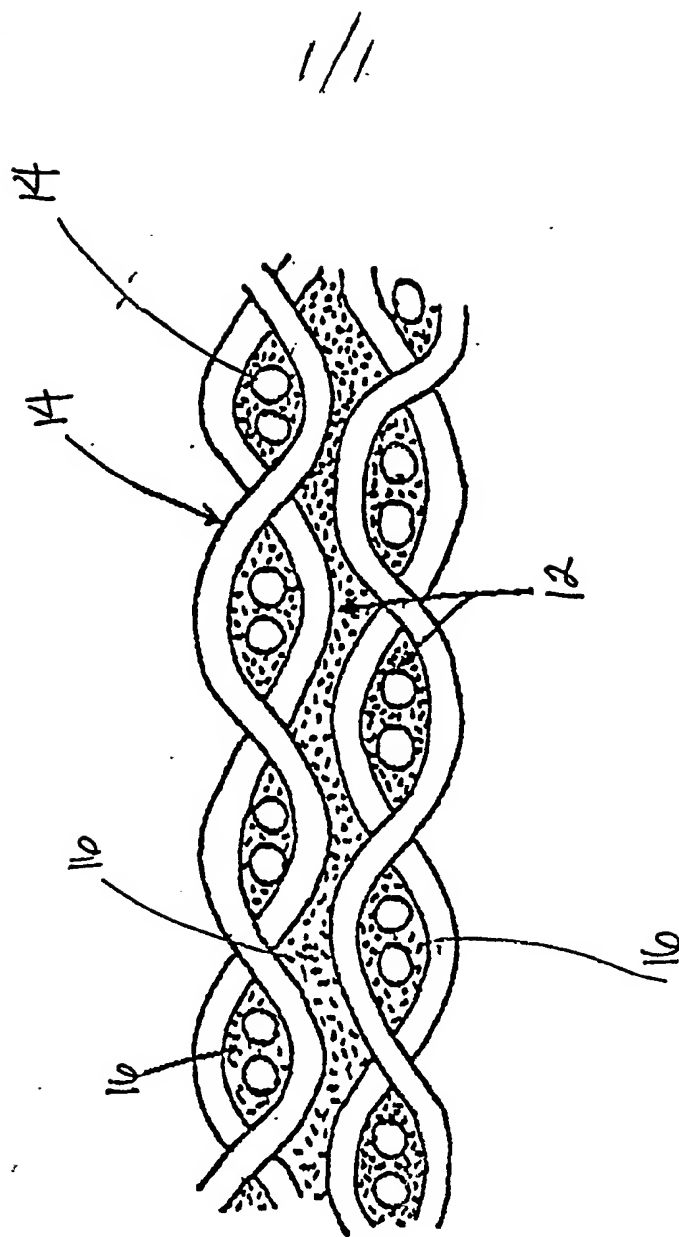


Fig. 1

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